PHYSICAL REVIEW B VOLUME 22, NUMBER 12 15 DECEMBER 1980

Study of crystalline electric fields in RD_2 (R = Tb, Dy, Ho, Er) using neutron inelastic scattering

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(Received 25 April 1979; revised manuscript received 19 May 1980)

Neutron energy-loss spectra of RD_2 (R = Tb, Dy, Ho, Er) were taken using powder samples on a triple-axis spectrometer. Excitations, believed to be crystalline electric-field (CEF) transitions were observed for all the compounds. In DyD_2, the observed transition energy is in good agreement with the CEF parameters derived from magnetic susceptibility and Mössbauer spectroscopy. The observed transitions in the spectra of HoD_2 and ErD_2 could not be fitted, taking into account the relative intensities, to any calculated scheme of cubic symmetry. With TbD_2, it was possible to fit the spectra to a calculated scheme and CEF parameters were deduced for $T > T_N$. However, these parameters failed to yield the correct T_N in the molecular-field calculations. Hence, a cubic CEF model is, in general, insufficient for describing the CEF transitions in RD_2.

I. INTRODUCTION

The crystal structure of RD_2 (R-rare earth) is cubic, of the fluorite type.[1] In this structure, the R ions form an fcc lattice. Each lattice point is a center of a cube of D ions. The R ion experiences, therefore, a simple cubic crystalline electric field (CEF). The CEF level schemes for Tb^{3+}, Dy^{3+}, Ho^{3+}, and Er^{3+} in cubic fields computed by Lea, Leask, and Wolf (LLW)[2] are presented in Fig. 1.

The cubic rare-earth deuterides (RD_2) exhibit interesting electronic and magnetic properties and have been studied by a variety of techniques. These properties are drastically affected by the crystalline electric field (CEF). Susceptibility,[3] specific heat[4,5] Mössbauer experiments,[6-10] neutron elastic scattering,[11,12] and inelastic scattering (NIS)[13-15] have been carried out to investigate the CEF interactions. All indirect CEF-level measurements[3-12] and the NIS measurement on PrD_2 (Ref. 13) lead to a model of hydridic hydrogen in a cubic CEF, while the NIS measurement on CeD_2 (Ref. 14) was inconsistent with such a model.

In this paper we report results obtained from NIS performed on RD_2(R = Tb, Dy, Ho, Er). Powder samples[16] and a triple-axis spectrometer were used in all the experiments.

II. EXPERIMENTAL AND ANALYSIS

Neutron energy-loss spectra of RD_2 (R = Tb, Dy, Ho, Er) were taken. Excitation transitions were observed for all the compounds. Common features to all the observed excitation lines in this study are as follows:

(i) The lines are relatively narrow, hence the excitations are at the most weakly dispersive.

(ii) The temperature dependence of the line intensities is consistent with that of CEF transitions.

(iii) The momentum-transfer (Q) dependence of the intensity is unlike the R^{3+} form factor (as expected of CEF transitions) but is rather Q independent.

Neutron energy-loss spectra were taken with an LaD_2 powder sample at 17 and 200 K (Fig. 2). As lanthanum is diamagnetic, this sample served as a blank for the four magnetic samples.

The LaD_2 spectra clearly demonstrate the absence of phonon contributions. Hence, we have no explanation for the Q dependence of the excitation intensities.

A. TbD_2

TbD_2 undergoes a phase transition from paramagnetism to antiferromagnetism at 17.2 K (Ref. 11) [16.1 K according to another study (Ref. 4)]. Mössbauer-effect measurements of Tb^{3+} in YD_2 in various dilutions lead to the conclusion of a nonmagnetic CEF ground state for the Tb^{3+} ion. Specific-heat results (Ref. 4) are consistent with the nonmagnetic Γ_2 level as ground state and $\Gamma_5^{(2)}$ about 50 K above it. A neutron elastic scattering study yielded[12] $X = 0.8$ and $W = -8.253$ K, i.e., Γ_2 as ground level and $\Gamma^{(2)}_5$ very close above it [Fig. 1(a)].

Two CEF transitions are observed in the NIS energy-loss spectra above T_N, having the energies of about 3.5 and 8 meV (Fig. 3). Below T_N, the energies of the transitions are shifted to higher values (4.7 and 10 meV respectively at 9 K). A

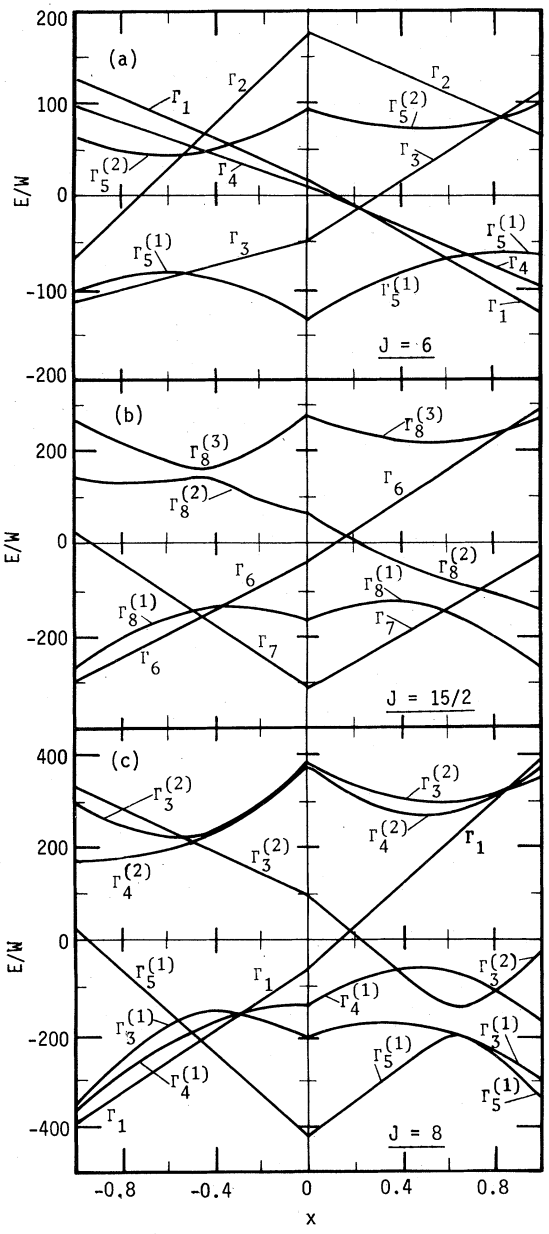

FIG. 1. Energy-level schemes for (a) Tb^{3+} ($J=6$), (b) Dy^{3+}, Er^{3+} ($J=\frac{15}{2}$), (c) Ho^{3+} ($J=8$) in a cubic CEF, taken from LLW (Ref. 2).

new transition line appears below T_N, and has the value of 6 meV at 9 K, probably due to splitting under the internal magnetic field either of the ground level or of the excited one.

Above T_N, the only values of the $J=6$ LLW scheme to which these transitions can be fitted are $X=0.43$ and $W=1.08$ K. The sign of W is inconsistent with tetrahedral or cubic coordination in the point-charge model.

The sublattice magnetization was calculated for these X, W values from

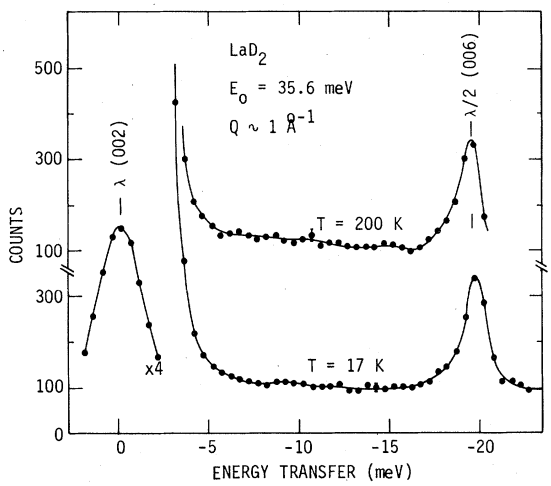

FIG. 2. Neutron energy-loss spectra of LaD_2. The elastic λ and $\lambda/2$ reflections of the (002) and (006) analyzer planes, respectively, are indicated. The solid lines are only guides to the eye.

$$M(H,T)=\frac{g\mu_B \mathrm{Tr}(J_z e^{-\mathcal{K}/kT})}{\mathrm{Tr}(e^{-\mathcal{K}/kT})},$$

where $\mathcal{K}=\mathcal{K}_{\mathrm{CEF}}-g\mu_B J_z H$, and H is the magnetic field. The results of these two-parameter (H and T) calculations are presented as a family of H/M isotherms (Fig. 4). In the molecular-field approxi-

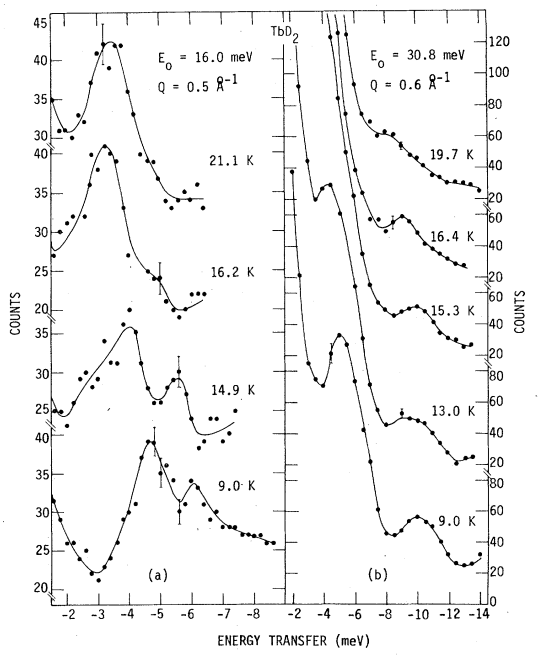

FIG. 3. Neutron energy-loss spectra of TbD_2 above and below T_N, at (a) neutron incoming energy 16.0 meV, (b) 30.8 meV. The −5-meV transition line is observed in the 30.8-meV spectra but the resolution is insufficient for the doublet separation.

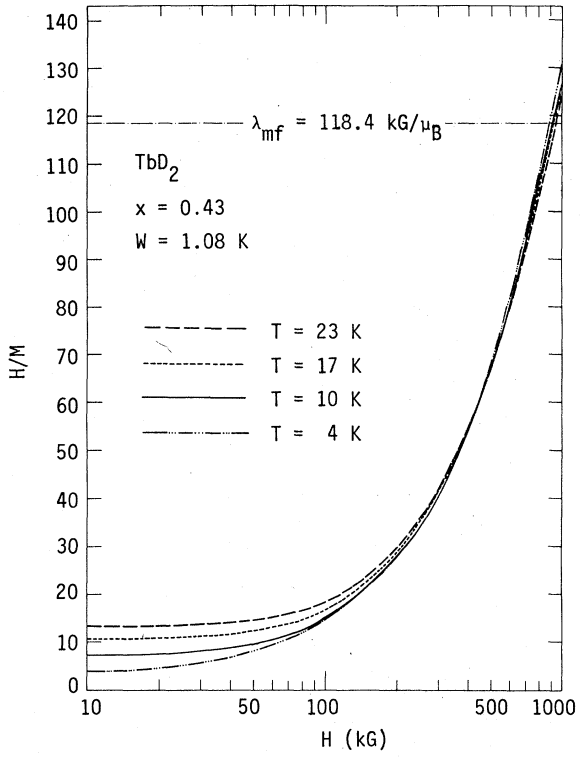

FIG. 4. Isotherms of H/M versus H (internal field) of the solution of the TbD_2 combined CEF and magnetic Hamiltonian for $X=0.43$ and $W=1.08$ K. The molecular-field constant value $\lambda_{mf}=118.4$ kG/μ_B corresponds to $7.6\mu_B$/Tb ion found by experiment (Ref. 11).

mation and in the absence of an external magnetic field, the sublattice magnetization-temperature curve is a solution of

$$\lambda_{mf}M(H,T)=H\ .$$

The experimental value of $7.6\mu_B$ at 4.6 K (Ref. 11) determines uniquely the molecular-field parameter at $\lambda_{mf}=118.4$ kG/μ_B. The magnetization-temperature curve is derived from the intersection points of the $\lambda_{mf}=118.4$ kG/μ_B curve with the H/M isotherms. It can easily be seen that the solution given in Fig. 4 does not give a physically meaningful magnetization-temperature curve,[12] besides the inconceivable value of 900 kG for the saturation internal field. The conclusion is, therefore, that there is no X value in the LLW scheme that can be fitted to the experimental energy values of the CEF transitions on both sides of T_N.

B. DyD_2

In a previous study,[9] an analysis of Mössbauer and magnetic-susceptibility data led to the following conclusions: (a) DyD_2 is antiferromagnetic, $T_N=3.3$ K, (b) the CEF ground state is Γ_7, and (c) the entire CEF level scheme is specified by the

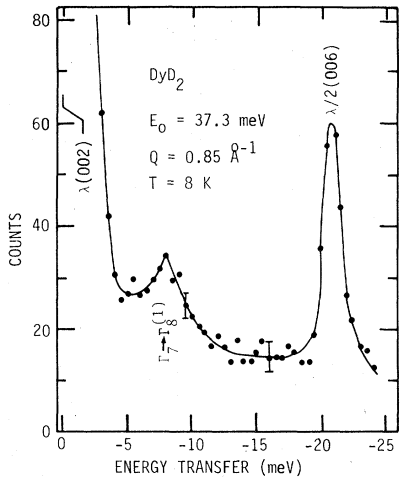

FIG. 5. Neutron energy-loss spectrum of DyD_2 at $T=8$ K. The expected $\Gamma_7\rightarrow\Gamma_8^{(1)}$ transition (Ref. 9) is indicated.

parameters $W=0.83\pm0.03$ K and $X=0.24\pm0.02$ [Fig. 1(b)]. The Schottky contribution to the specific heat calculated with these CEF parameters is in agreement with experiment.[5] At 8 K (paramagnetic state) a transition line was observed at about −8 meV (Fig. 5),[17] in excellent agreement with the $\Gamma_7\rightarrow\Gamma_8^{(1)}$ transition in the previously predicted CEF level scheme [Fig. 1(b)]. This transition has a large transition-probability matrix element.[18] The $\Gamma_7\rightarrow\Gamma_8^{(2)}$ transition at about

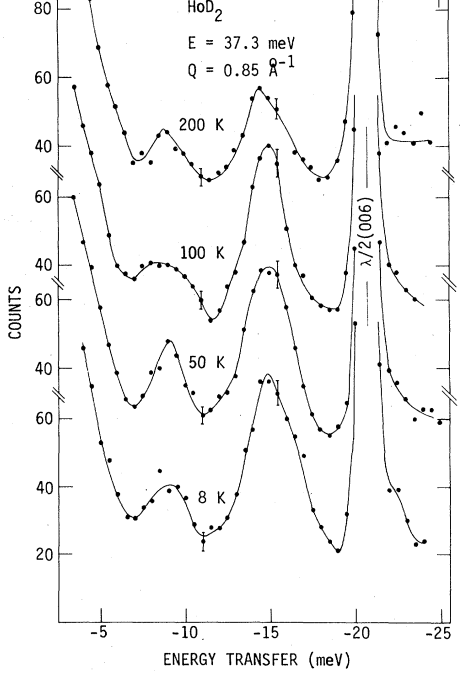

FIG. 6. Neutron energy-loss spectra of HoD_2.

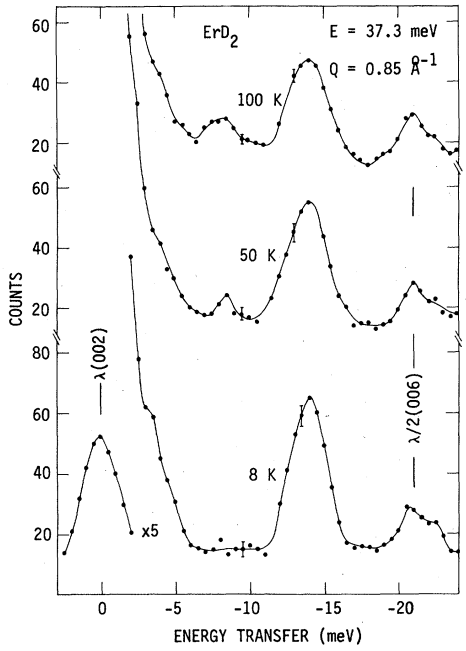

FIG. 7. Neutron energy-loss spectra of ErD_2.

16 meV has a very small transition probability and is not observed. The $\Gamma_7 \rightarrow \Gamma_6$ transition is forbidden.

A spectrum was obtained at 100 K where $\Gamma^{(1)}$ is populated. Broad weak lines in this spectrum can be associated with $\Gamma_7 \rightarrow \Gamma_8^{(1)}$, $\Gamma_8^{(1)} \rightarrow \Gamma_8^{(2)}$, and $\Gamma_8^{(1)} \rightarrow \Gamma_6$ transitions.

C. HoD_2

HoD_2 undergoes a phase transition to an antiferromagnetic state at $T_N \sim 5.2$ K.[10] Energy-loss spectra were taken at several temperatures above T_N (Fig. 6). Two transition lines are observed at about −9 and −15 meV, and the constant intensity ratio implies that these are transitions from the ground state to two excited ones. Considering, even qualitatively, the expected-intensities ratio of transitions[18] from every possible ground state to two excited states, in the LLW scheme [Fig. 1(c)], there is no X value that can be fitted to the observed transitions.

D. ErD_2

ErD_2 undergoes a phase transition to an antiferromagnetic state at $T_N = 2.3$ K.[10] Energy-loss spectra were taken at three temperatures above T_N (Fig. 7). Three transition lines were observed at about −3.5, −8.5, and −14 meV. [The −3.5-meV transition was better resolved from the elastic peak by lower-energy incoming neutrons (not shown).] Their temperature dependence implies that the transitions at −3.5 and −14 meV are from the ground state to two excited ones, while the −8.5-meV transition is from an excited state to a higher one. The −8.5- and −14-meV transition lines were observed in a former NIS study[19] and fitted to X, W values in the LLW scheme [Fig. 1(b)]. No X value can, however, be found in the LLW scheme [Fig. 1(b)] so that the three observed transition energies will fit the calculated ones.

III. DISCUSSION

CEF transition lines were observed in the NIS energy-loss spectra of RD_2 (R = Tb, Dy, Ho, Er). Only the DyD_2 spectrum can be fitted to the LLW scheme of CEF levels, and the X, W values obtained are in excellent agreement with those obtained by indirect methods.[9] The TbD_2, HoD_2, and ErD_2 spectra cannot be fitted to the respective LLW schemes for any X value. It has to be noted that the 8-K spectrum of DyD_2 yielded only one transition line, which can be fitted anyway to any scheme and the agreement of the observed transition to the reported X, W might be accidental. The only other published direct NIS study on RD_2 where the observed data were fitted to calculated CEF parameters was on PrD_2 (Ref. 13) where, too, only one transition line was observed. The transitions observed in the CeD_2 study[14] could not be, however, fitted to the LLW scheme.

It seems, therefore, that the CEF transitions of the RD_2 system cannot, in general, be explained within the assumption of CEF of cubic symmetry. For CeD_2 it was found[20,21] that a few percent of the tetrahedral sites are vacant, the excess hydrogens entering octahedral sites and thus introducing a perturbation on the cubic field. This possibility should be checked for the compounds of this study.

ACKNOWLEDGMENT

The authors wish to thank H. Ettedgui for his technical assistance.

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